Int. J. Electrochem. Sci., 5 **(2010)** 1634 - 1648

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Study of Electrocatalytic Oxidation of Isoniazid Drug Using Alizarin Red S as A Mediator on the Glassy Carbon Electrode

Mohammad Ali Karimi[1,2,*], *Abdolhamid Hatefi-Mehrjardi*[1], *Mohammad Mazloum-Ardakani*[3], *Reza Behjatmanesh-Ardakani*[2], *Mohammad Hossein Mashhadizadeh*[4], *Shahnaz Sargazi*[2]

[1] Department of Chemistry & Nanoscience and Nanotechnology Research Laboratory (NNRL), Payame Noor University (PNU), Sirjan, Iran
[2] Department of Chemistry, Faculty of Science, Payame Noor University (PNU), Ardakan, Iran
[3] Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran
[4] Department of Chemistry, Tarbiat Moallem University of Tehran, Tehran, Iran
[*]E-mail: ma_karimi43@yahooo.com; m_karimi@pnu.ac.ir

Received: 5 August 2010 / *Accepted:* 15 September 2010 / *Published:* 1 November 2010

The anodic oxidation of isoniazid (INH) has been studied on the glassy carbon electrode by electrocatalytic effect of Alizarin Red S (ARS) as a homogenous mediator in phosphate buffer (pH = 6). The linear sweep voltammetry (LSV) studies showed that the catalytic current of this system depends on the concentration of INH. The magnitude of the peak current for ARS increased severely in the presence of INH, and proportional to the concentration of INH. The obtained catalytic peak current was linearly dependent on the INH concentration in the range of 10-800 µmol L^{-1} and the detection limit of 3.94 µmol L^{-1} by LSV and in the range of 0.05-0.85 µmol L^{-1} and the detection limit of 0.0163 µmol L^{-1} by differential pulse voltammetry (DPV). The method also was used for estimation of the catalytic rate constant at catalytic reaction between ARS and INH. The influences of potentially interfering substances on the current response of the system were examined. The importance of the technique is because of its ability to electrocatalytic determination of INH with ARS as homogenous electrocatalyst, while it does not need to be prepared as for the modified electrode. The method was successfully applied for analysis of INH in solid pharmaceutical formulations.

Keywords: Electrocatalytic oxidation, Homogenous mediator, Isoniazid, Alizarin red S, Glassy carbon electrode

1. INTRODUCTION

Tuberculosis is one of the leading causes of death worldwide. Isonicotinic acid hydrazide (INH), or Pyridine-4-carboxylic acid hydrazide, commercially known as isoniazid (INH), is one of the

most important drugs that are widely used in manufacturing pharmaceuticals and agrochemicals along with rifampicin and pyrazinamide in the chemotherapy of the disease[1-2]. INH has been in use for about five decade and owing to its importance, considerable attention has been paid to the study and determination of INH in recent years. Reported analytical techniques for the determination of INH include capillary electrophoresis with electrochemical detection [4,5], visible spectrophotometry [6-11],UV spectrophotometry [12], spectrofluorimetry [13-14], chemiluminescence [15-21], colorimetry [22,23], titrimetry [22-25], and chromatography [26-30]. In addition, a variety of electrochemical techniques such as amperometry [31], polarography and voltammetry [32-35], at different electrode materials such as an ion-selective electrode (ISE) [36], gold [37], platinum [38], hanging mercury dropping electrode (HMDE) [39], glassy carbon electrode (GCE) [31], carbon paste electrode (CPE) [40], and different chemically modified electrodes (CMEs) with multi-wall carbon nano tubes (MWNTs) [41,42], overoxidized polypyrrole (OPPy) film [43], poly(amidosulfonic acid) (PASA) [44], and some of chemometrics methods such as partial least-squares (PLS), genetic algorithm partial least squares (GA-PLS), and artificial neural networks (ANNs) have been utilized in the electrochemical oxidation and determination of INH [45,46]. It is desirable to have an unmodified electrode to oxidize INH at neutral pH with high efficiency. The requirement of electrode modification or electrochemical pretreatment steps should also be avoided in order to allow the frequently and repeatedly use of the electrode. A study on the kinetics and mechanism of the electrocatalytic oxidation by 2,2,6,6-tetramethyl-4-acetylpiperidine-1-oxyradical and the homogeneous oxidation of INH by N-haloarenesulfonamidates have been reported [47].

In the previous works we used Alizarin Red S (ARS) as a homogenous mediator on the hydroxylamine and hydrazine determinations [48,49]. It seems that catalytic oxidation reaction of INH in the presence of ARS is performing. The present work is intended to description of the response and suitability of ARS as a new homogenous mediator in the electrocatalysis and determination of INH in an aqueous solution, and then evaluation of the analytical performance of the homogenous electrocatalyst in the quantification of INH.

2. EXPERIMENTAL

2.1. Reagents

Alizarine Red S (1,2-Dihydroxyanthraquinone-3-sulfonic acid disodium salt), and isoniazid (Pyridine-4-carboxylic acid hydrazide) were obtained from Merck® and used as supplied. All solutions were prepared with analytical-reagent grade chemicals and were used as received from the suppliers without further purification and by using doubly distilled water. INH and ARS solutions were freshly prepared just prior to use and all experiments were carried out at ambient temperature. Tablets of INH (Darou Pakhsh, Iran) were purchased from local pharmacies. In the optimized conditions phosphate buffer solution (80 mmol L^{-1}, pH = 6.0) were used. Phosphoric acid and sodium hydroxide were used for increasing and decreasing the pH of the buffer.

2.2. Apparatus

A conventional three-electrode cell, consisting of glassy carbon disk electrode (PINE AFE2M050, 5.0 mm) as working, Ag/AgCl, 3 M KCl as reference, and platinum wire as auxiliary electrode, connected to the electrochemical system, Autolab® PGSTAT 302 (Eco Chemie B.V., The Netherlands), interfaced with a personal computer was used for electrochemical measurements. All potentials in this work are reported versus the reference electrode. The electrochemical data acquisitions were performed using GPES 4.9 software. A Metrohm 781 pH/Ion meter was also used for pH measurements.

2.3. Procedure

The glassy carbon working electrode surface was successively polished to a mirror-finish using aqueous slurries of alumina (0.05 µm, Buehler®) followed by rinsing thoroughly with twice-distilled water. Then the electrodes were transferred into the electrochemical cell that containing buffer solution, and 0.1 mol L^{-1} ARS. The potentials were swept from +0.1 V to +0.8 V *vs.* Ag/AgCl, and then reversed with a scan rate of 250 mVs^{-1}. The experiment was repeated in the presence of INH as a sample. The cyclic voltammograms of blank and sample solutions give the blank signal (I_b) and analytical signal (I_s). The difference between the blank and analytical signal ($I_p=I_s-I_b$), was proportional to INH concentration. Calibration graphs were obtained by plotting the net peak current (I_p) against standard concentration of INH.

3. RESULTS AND DISCUSSION

3.1. Electrocatalytic oxidation of isoniazid

3.1.1. Voltammetry measurements

The catalytic oxidation of INH in the presence of ARS can be observed clearly in the electrochemical response. The experiments showed that ARS can be act as a suitable mediator of the electron transfer during the oxidation of INH. The peak current of ARS increased sharply in the presence of INH and the peak potential of ARS is at the lower potential than that for the INH. The basis of redox catalysis is the replacement of electron transfer at the electrode by that occurring in the solution. Therefore, the electrochemical methods, for the determination of INH, are based on the following sequence of reactions:

$$\text{ARS}_{(aq,red)} \rightarrow \text{ARS}_{(aq,ox)}$$

$$\text{ARS}_{(aq,ox)} + \text{INH}_{(aq,red)} \rightarrow \text{ARS}_{(aq,red)} + \text{INH}_{(aq,ox)}$$

The first reaction have been occur at the surface of glassy carbon electrode, then in the presence of INH, the oxidized mediator can be oxidize INH and converts to its initial form, while the ARS itself can be oxidized further, so the peak current of ARS increases in the presence of isoniazid. The rates of the two reactions are, however, not independent from one another and the prediction of the catalytic efficiency relies upon the relationship between them. The cyclic voltammograms obtained on a bare glassy carbon electrode in phosphate buffer solution (80 mM, pH 6.0), in the absence and presence of INH, are shown in Fig. 1 (curves a, and b). This shows the electrooxidation of INH requires a large anodic overpotential. The same cyclic voltammograms in the presence of ARS are also overlaid on Fig.1 (curves c, and d).

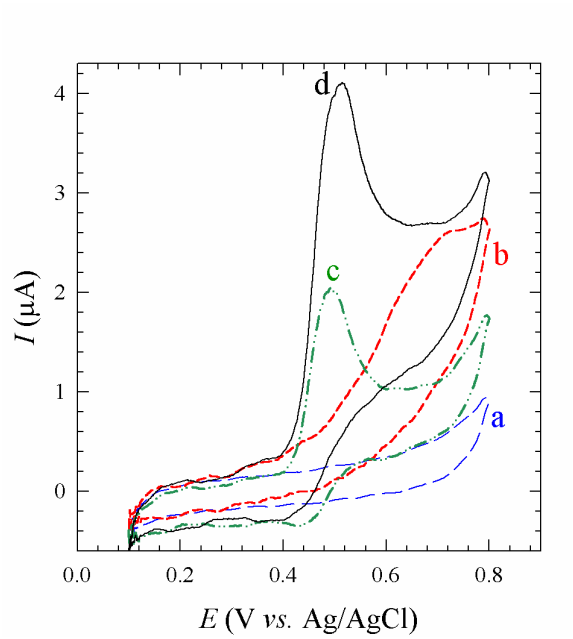
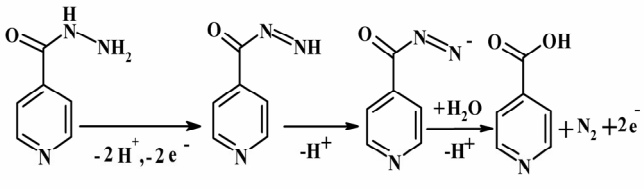


Figure 1. Cyclic Voltammograms of glassy carbon electrode in 80 mM phosphate buffer solution (pH 6.0) with a scan rate of 250 mVs^{-1}: (a) in the absence of INH; (b) in the presence of 0.1 mM INH; (c) in the presence of 0.1 mM ARS and (d) in the presence of 0.1 mM INH and 0.1 mM ARS.

Addition of ARS to the cell in the presence of INH produced a dramatic change in the cyclic voltammograms. As is well known, the increment of catalytic current and the decrease in overpotential are the two important factors in evaluating the catalytic effect [50,51]. In the presence of ARS with the INH, a large anodic peak was recorded. The current, observed during the experiment, was associated with the INH oxidation and demonstrated by comparing the current in Fig. 1 (curve d) with that in Fig. 1 (curve c), which shows the CV behavior of an electrode in 0.1 mM ARS solution in an INH-free solution. These results, obtained from cyclic voltammetry, lead to the conclusion that the overall electrochemical oxidation of INH under these conditions might be controlled by the diffusion of INH in the solution (diffusion layer of the ARS). Therefore, the I_p depends on the INH concentration.

The electrochemical oxidation of INH was studied by means of DC and differential-pulse polarography, linear sweep and cyclic voltammetry in the pH range 6-13 [52]. The oxidation processes were found to be of the ECE type where the rate-determining step was the release of an H^+ ion from the intermediate formed after two reversible one-electron transfers. The electroreduction of INH was studied on the mercury electrode in acidic media of pH<6 and in natural and basic media [53,54]. The oxidation mechanism at the electrode can be written as shown on the Scheme 1.



Scheme 1. The electro-oxidation mechanism of INH at the electrode surface.

Figure 2 shows the linear sweep voltammogram of blank solution, containing ARS (0.1 mmol L^{-1}) in 80 mmol L^{-1} phosphate buffer (pH 6.0), at the sweep rate of 2 mVs^{-1}. The points show the rising part of voltammogram which is known as Tafel region and is affected by the electron transfer kinetics between INH and ARS, assuming the deprotonation of INH as a sufficiently fast step. In order to get information on the rate determining step a slope of 103.57 mV/decade is obtained indicating that the process follow two electron transfer in rate determining step assuming a transfer coefficient of α = 0.577 [43,55].

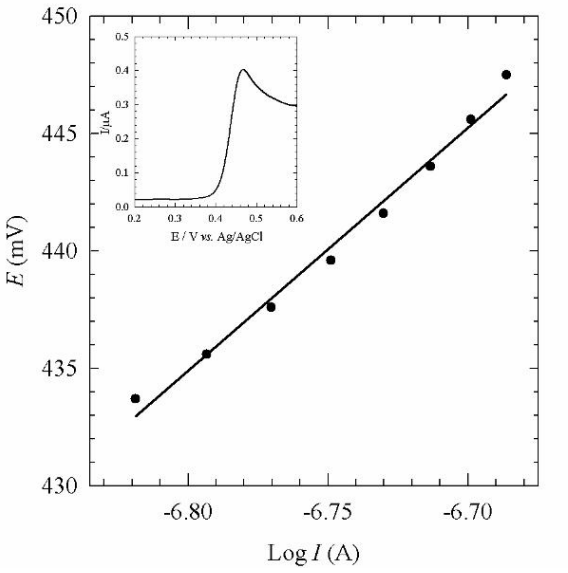


Figure 2. A Tafel plot of glassy carbon electrode in 80 mM phosphate buffer (pH 6.0), 0.1 mM ARS, with a scan rate of 2 mV/s. Inset shows the corresponding linear sweep voltammogram.

3.1.2. Influence of variables

The influence of chemical variables such as pH, ARS concentration, and scan rate on sensitivity was studied on the peak current. The results showed that the pH affects the electrochemical behavior of ARS and also INH activity. From Fig. 3, it can be seen that the pH value of buffer medium has an important effect on the efficiency of the electrocatalytic oxidation of INH.

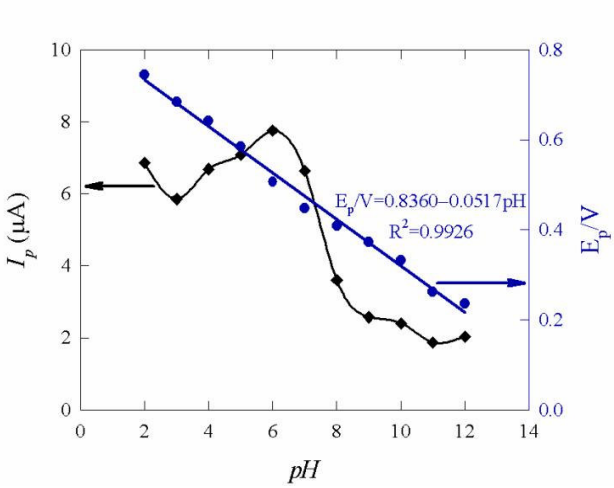


Figure 3. Variation of the I_p and E_p of INH (0.1 mM) with pH. Scan rate was 250 mV/s.

We found that the buffer medium with the pH 6.0 showed significant results, so this medium was chosen for the subsequent experiments. As can be seen in Fig. 3 the peak potential is pH dependent, with a slope of -51.7 mV/pH unit in a wide range, which is very close to the expected Nernstian value of 59 mV for a "two electron-two proton" process.

The effect of pH on the electrocatalytic oxidation of INH was also observed in the presence of 0.1 mmol L^{-1} ARS as shown in Fig. 4.

The peak current was increased by increasing the pH from 3.0 to 6.0, and then decreased for higher pH values. However the higher peak current and better shape of the voltammogram peak at pH 6.0 suggested this pH as the optimal pH value for the purpose.

The influence of ARS concentration on the anodic peak currents was studied for the concentration range of 1.0-260 mmol L^{-1} ARS, in the solutions containing different concentrations of INH at pH 6.0 (Fig. 5).

The results showed that by increasing ARS concentration up to 100 mmol L^{-1} the peak current increased, whereas higher concentration of ARS caused a slight increase on the magnitude of peak current, due to the formation of ARS aggregation. Therefore, 100 mmol L^{-1} ARS concentrations were selected as the optimal mediator concentration.

The scan rate dependence of cyclic voltammograms on the glassy carbon electrode in 80 mM phosphate buffer solution containing 0.10 mmol L^{-1} ARS and different concentrations of INH (data not

shown) was used to get the information about the rate determining step. Fig. 6, curves a-c, shows the linear relationship between anodic peak current *versus* the square root of the sweep rate.

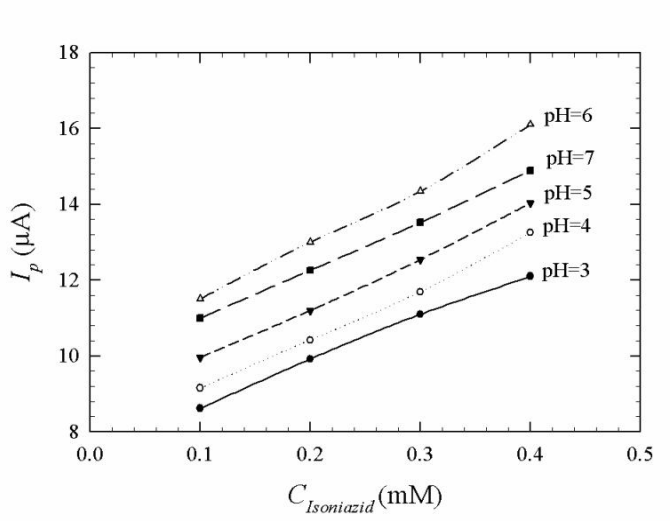


Figure 4. Influence of pH on the electro-oxidation of different INH concentrations at a glassy carbon electrode in the presence of 0.1 mM ARS (scan rate: 250 mVs^{-1}) with the potential range of +0.30 to+0.74 V *vs.* Ag/AgCl.

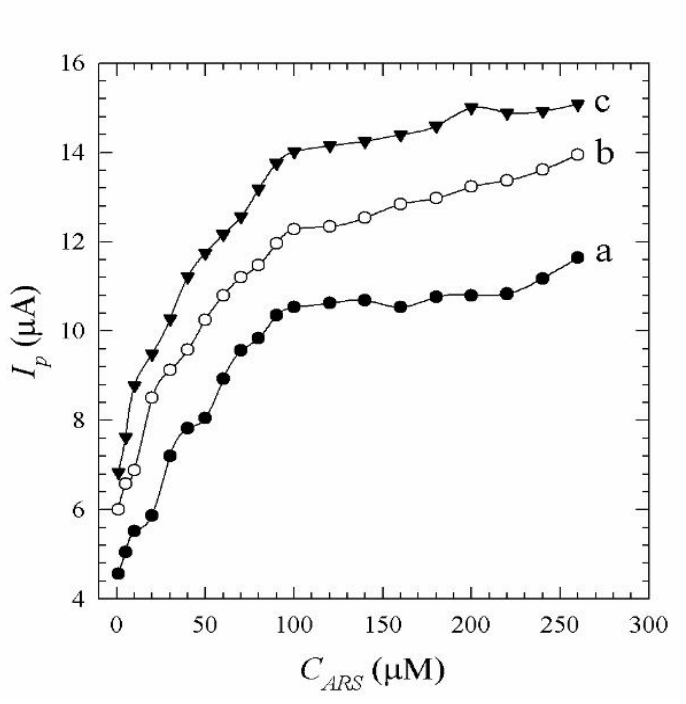


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Figure 5. Effect of ARS concentration on the electro-oxidation of different INH concentrations (a) 0.1, (b) 0.2, and (c) 0.3 mM where pH of the phosphate buffer is 6.0 and scan rate is 250 mVs^{-}

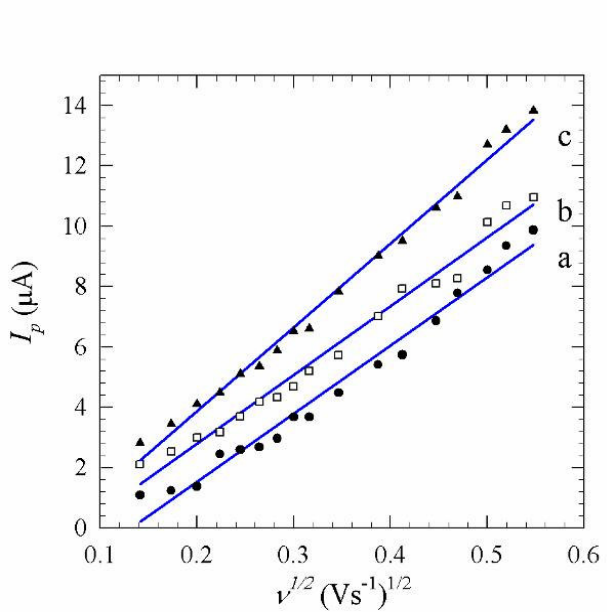

Figure 6. Variations of the CV anodic peak current with the square root of scan rate in the presence of different concentrations of INH: (a) 0.1, (b) 0.2, and (c) 0.3 mM at pH 6.0 and 0.1mM ARS.

From the slope of the I_p *versus* $\upsilon^{1/2}$, the number of electrons in the overall reaction can be obtained. This behavior suggests that the oxidation process is controlled by diffusion, according to the following equation for a totally irreversible diffusion controlled processes [56]:

$$I_p = 3.01\times10^5 n[[(1-\alpha)]n_\alpha]^{1/2} A C_b D^{1/2} \upsilon^{1/2} \qquad (1)$$

Considering $[(1-\alpha)]n_\alpha = 0.846$, $C_b = 60$ mmol L^{-1}, $D = 3.06 \times 10^{-6}$cm^{2}s^{-1} (D was calculated by chronoamperometry), and A=0.196 cm^2 the number of electrons in anodic oxidation of INH is $n = 3.96$ ($n \cong 4$). A plot of the sweep rate-normalized current ($I_p/\upsilon^{1/2}$) *versus* sweep rate exhibits the characteristics shape typical of an EC' catalytic process [55].

3.2. Chronoamperometry measurements

Chronoamperometry measurements were performed at a constant applied DC potential on glassy carbon electrode in 80 mmol L^{-1} Phosphate buffer, pH 6, containing 0.1 M ARS, and different amount of INH added to the solution. Thus, the potential of the working electrode held at +0.600 V *vs.* Ag/AgCl where ARS oxidation current is controlled by mass diffusion, INH was added stepwise to the solution and the current was monitored. The chronoamperograms obtained on a series of INH concentrations are illustrated in Fig. 7A.

It can be seen that an increase in concentration of INH was accompanied by an increase in anodic currents. In the presence of INH at long times (t>4s), the ARS oxidation is completed and the

rate of INH electrocatalyzed oxidation exceeds that of INH diffusion from the bulk to the ARS (formerly diffused to the electrode surface), and therefore the current has diffusional nature. In chronoamperometric studies, the diffusion coefficient of INH can be determined. The relationship between diffusion coefficient and bulk concentration can be describe by the Cottrell equation [55]:

$$I = nFAD^{1/2}C_b/\pi^{1/2}t^{1/2} \qquad (2)$$

Where D and C_b are diffusion coefficients (cm^2s^{-1}) and the bulk concentration ($molcm^{-3}$), respectively. The level of Cottrell current measured for the first 40 s, increased with increasing INH concentration. From the Cottrell equation it can be seen that the plot of I *vs.* $t^{-1/2}$ under diffusion control is linear, and from the slopes, the value of D can be obtained.

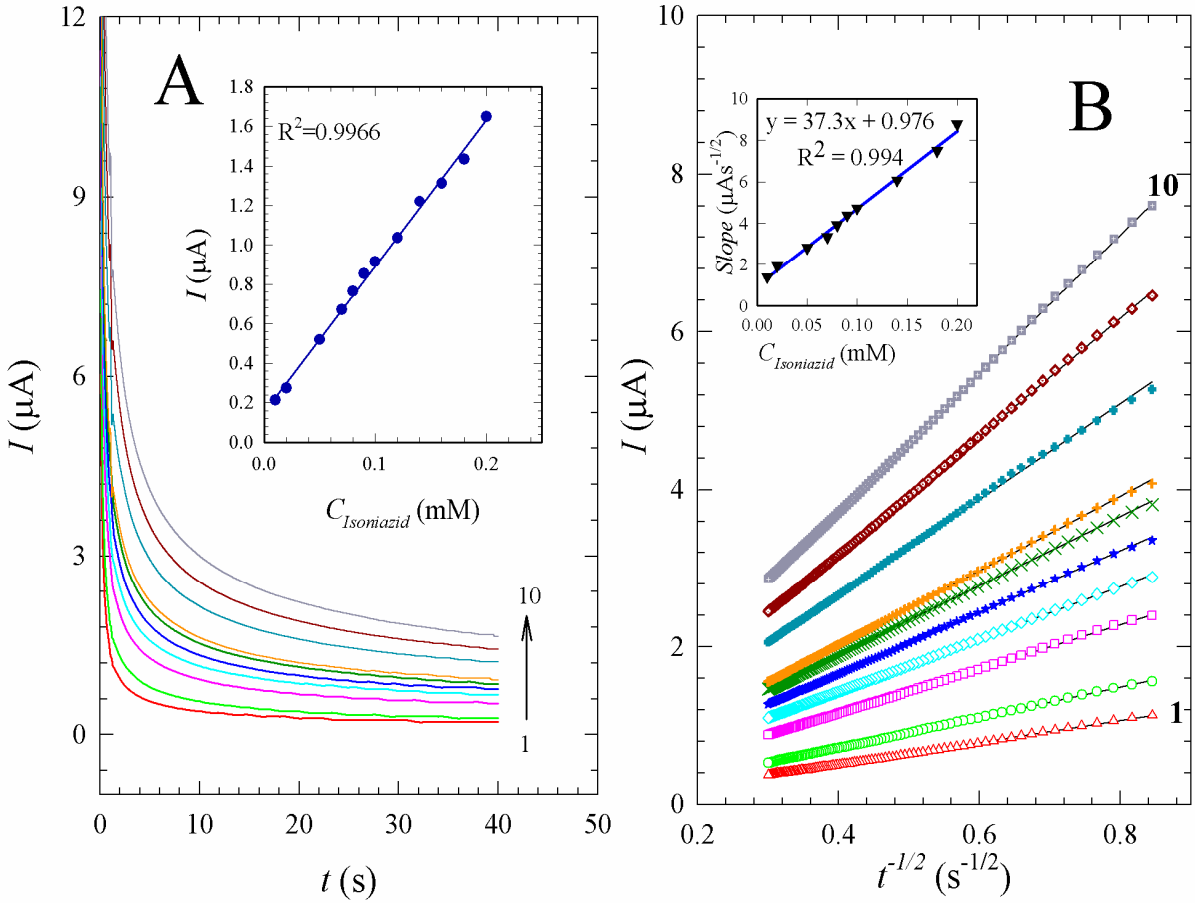

Figure 7. (A) Chronoamperometric response of the GC electrode in 80 mM phosphate buffer, pH 6, containing 0.1 mM ARS, and different concentrations of INH for a potential step of +0.600 V *vs.* Ag/AgCl. The numbers 1 to 10 correspond to 10, 20, 50, 70, 80, 90, 100, 140, 180, and 200 µM of INH, respectively. Inset shows the variation of chronoamperometric currents at t=40 s *vs.* INH concentration. **(B)** Plot of I *vs.* $t^{-1/2}$ obtained from chronoamperograms (A) for the same concentrations of INH. Inset shows the relationship between the slopes of the lines and concentrations.

Fig. 7B shows the experimental plots for different concentrations of INH employed. The slopes of the resulting straight lines were then plotted *vs*. the concentration of INH (Fig. 7B), from which we calculated a diffusion coefficient of 3.06×10^{-6} cm^2s^{-1} for INH, which is in good agreement with values reported in literature [43].

Chronoamperometry studies can be done to evaluate the catalytic rate constant. At intermediate time (1.5-4 s in present work) the catalytic current (I_{cat}) is dominated by the rate of electrocatalyzed oxidation of INH. So the rate constant for the chemical reaction between INH and oxidized form of ARS is determined according to the method described in the literature [55]:

$$I_{cat}/I_d = \gamma^{1/2}[\pi^{1/2}\,\mathrm{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2}] \qquad (3)$$

Where I_{cat} and I_d is the currents of ARS in the presence and absence of INH, respectively. $\gamma = k'C_0t$ (C_0 is the bulk concentration of INH (mmol L^{-1}), k' is the catalytic rate constant (L mol^{-1} s^{-1}) and t is time elapsed (s)), and erf ($\gamma^{1/2}$) is the argument of error function. In treatments, it is assumed that INH is present in large excess rather than ARS. For γ>1.5, erf($\gamma^{1/2}$)$\rightarrow$1, exp(-γ)/$\gamma^{1/2}\rightarrow$1, and the above equation can be considered as follows:

$$I_{cat}/I_d = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(k'C_0t)^{1/2} \qquad (4)$$

The slope of I_{cat}/I_d *vs*. $t^{1/2}$ for 0.20 mM INH was determined and k' was calculated to be $1.22\times10^{+3}/M^{-1}s^{-1}$ (Fig. 8).

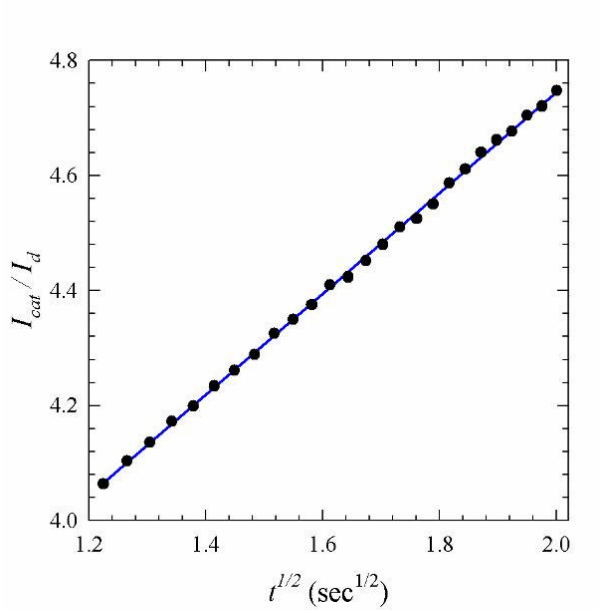

Figure 8. The plot of I_{cat}/I_d *vs*. $t^{1/2}$ from chronoamperometry for 0.2 mM INH at optimum conditions for catalytic rate constant (k') evaluation

3.3. Analytical application

3.3.1. Calibration and detection limit

Under the optimum conditions, the calibration curve was obtained by linear sweep voltammetry (LSV) method from 10 to 800 μM INH (Fig. 9). The peak currents were extracted and plotted *versus* concentration [i_p/μA = 7.48(±0.19) + 1.69(±0.04) × 10^{-2}C/μM, r^2 = 0.988].

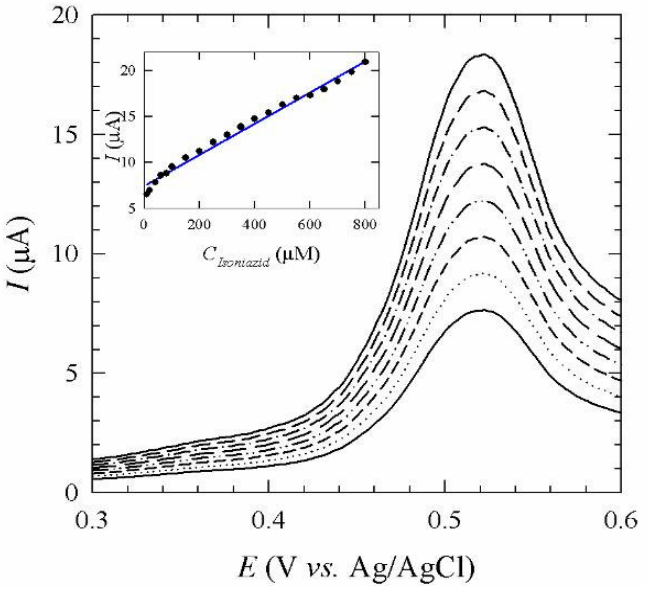

Figure 9. Linear sweep voltammograms obtained on the glassy carbon electrode from 10 to 800 μM INH in 80 mM phosphate buffer solution, pH 6.0, containing 0.1 mM ARS, with a scan rate of 250 mV/s. Inset shows calibration curve obtained from variation of peak current as a function of INH concentration.

The detection limit, calculated from the standard deviation of the background (signal equals 3*S* where *S* was the standard deviation of background for 10 measurements), was 3.94 μM, and the relative standard deviation (%RSD) for 5 replicated analysis of 20 and.40 μM INH were 0.85% and 1.14%, respectively. Also more sensitive method, *i.e.* differential pulse voltammetry (DPV) was studied for INH determination at the lower concentration. Under the same solution conditions, the calibration curve was obtained by DPV method from 0.05 to 0.85 μM INH (Fig. 10). The peak currents were extracted and plotted *versus* concentration [i_p/μA = 19.91(±0.09) + 17.07(±0.23) × C/μM, r^2 = 0.997]. The detection limit of 0.0163 μM was obtained from the DPV blanks (n=10).

3.3.2. Interference studies

Possible interferences in the LSV determination of 0.1 mM INH were examined under the optimum experimental conditions. The limit of the potential interfering substances was defined as

error-less than 3% in determination of 0.1 mM of INH concentration. The results; showed that the peak current of 0.1 mM INH was not affected by 1000-fold of Na^+, NH_4^+, PO_4^{3-}, HCO_3^-, NO_3^-, glucose, galactose, lactose, sorbitol, sodium citrate, nicotinic acid, and thiamine hydrochloride, 25-fold of ascorbic acid, and one-fold of riboflavin for LSV measurements. Only riboflavin has maximum effect on the determination of INH. While almost all of other cations and anions have no effect.

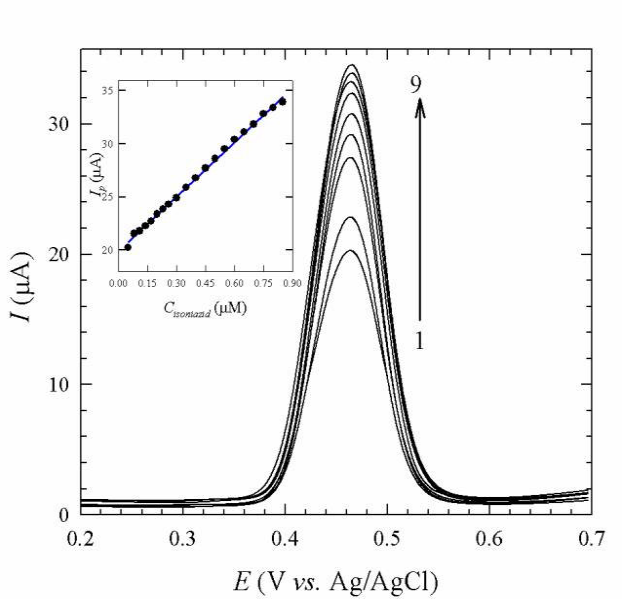

Figure 10. Differential pulse voltammograms of the glassy carbon electrode in 80 mM phosphate buffer solution, pH 6.0, containing 0.1 mM ARS. The numbers 1 to 9 correspond to 0.05, 0.17, 0.40, 0.50, 0.60, 0.70, 0.75, 0.80, and 0.85 µM of INH, respectively. Inset shows calibration curve obtained from variation of peak current as a function of INH concentration.

Table 1. Recovery of INH from two pharmaceutical samples

Sample[a]	Founded (mg)[b] (Proposed method)	Official BP method	*t*-value[c]	*F*-Value[d]
Tablet (100 mg)	99.5±0.85 (n=6)	100.8±1.0 (n=6)	1.31	1.38
Tablet (300 mg)	**306.8±0.45 (n=6)**	**307.5±0.8 (n=6)**	**3.30**	**3.16**

[a] Samples were INH tablets of Iran Daru Pakhsh.
[b] Average values of five determinations ± standard deviation.
[c] Tabulated value at 95% confidence level is 2.31.
[d] Tabulated value at 95% confidence level is 6.39.

3.3.3. Real sample analysis

The proposed method was used for the direct determination of INH in pharmaceutical sample. The recoveries of the INH are determined by the standard addition method. The results are presented in Table 1. The results were compared with those obtained by the British Pharmacopoeia (BP) official method [57]. A standard method (BP) was used to check the accuracy of the proposed method. These results suggest that the proposed method is very reliable and sensitive with regard to determination of INH in pharmaceutical samples.

4. CONCLUSIONS

ARS exhibited excellent electro-catalytic behavior toward the INH oxidation in the aqueous phosphate buffer solution on a bare glassy carbon electrode. The process is pH dependent and the highest catalytic current is observed at pH 6.0, which is close to the neutral pH. This technique offers certain advantages over the conventionally modified glassy carbon electrodes especially, in its simplicity because it does not need to be prepared as for the modified electrodes. The anodic oxidation of INH by ARS was totally irreversible and diffusion-controlled with N_2, as the final product. On the basis of Tafel plot and the consideration of the charge transfer step of the rate–limiting reaction, which was a two-electron-process, the transfer coefficient (α) was 0.577. The other kinetic parameters such as, catalytic reaction rate constant (k') and the diffusion coefficient were also determined using the chronoamperometry. The sensor developed for the determination of INH was very rapid (less than 1 min per sample solution), reproducible, highly selective and sensitive, and can be used for real sample analysis. The importance of the method is its ability for electrocatalytic determination of the INH in high and very low concentrations by voltammetry techniques such as LSV and DPV methods respectively. The method is successfully applied for the determination of INH in the pharmaceutical.

ACKNOWLEDGEMENTS
The authors are thankful to the Payame Noor Universities of Ardakan and Sirjan, to IUT research council and Center of Excellence in Sensors for support of this work.

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